Comment on "How Water Meets a Hydrophobic Surface"

The prediction of a low-density depletion layer at the boundary between water and a hydrophobic surface has attracted significant theoretical and experimental attention [1–5]. Recently, Poynor *et al.* [4] have carried out a "tour de force" x-ray reflectivity experiment which allowed them to deduce an electron density depletion at the interface of water in contact with the hydrophobic methyl-terminated octadecyltriethoxysilane (OTE) surface. From their analysis, they determined the presence of a $2–4$ Å-thick depletion layer with an electron density $\leq 40\%$ that of bulk water [4]. They state that "the quantification of the radii of the methyl protons appears to be subjective," and they do not attribute part of the depletion to the low density of the methyl groups. Rather, their entire calculated electron density depletion is attributed to a depletion of water. Here we show that a similar low electron density depletion is observed in other systems with interfacial methyl groups [6,7]. Using these results as a basis for our reanalysis, the water deficit reported by Poynor *et al.* is significantly reduced.

The x-ray reflectivity measurements do not have the sensitivity to independently determine the depletion density ρ_{dep} and the thickness of the depletion zone δD, and, in such cases, it is possible only to accurately determine the density difference $\Gamma = \delta D \delta \rho$ [8]. Here $\delta \rho = \rho_{\text{avg}} - \rho_{\text{dep}}$, where ρ_{avg} is the electron density of the methylene region. Therefore, we now focus on the value of Γ for several relevant systems (see Table I). In bulk crystalline alkanes, Craievich, Denicolo, and Doucet [6] obtain a depletion layer for the methyl group regions between the molecular layers from x-ray crystallography, and this yields $\Gamma = 0.58\ e\text{Å}^{-2}$. In the methyl-rich region between lipid bilayers, the electron depletion corresponds to the equivalent length of $1.75–2.0$ CH$_2$ groups [7] corresponding to $\Gamma = 0.56\ e\text{Å}^{-2}$, in close agreement with the alkane result. In both the alkane and the lipid cases, the depletion for each half of the bilayer is a factor of 2 smaller. For the OTE/water interface, acceptable fits were obtained with a range of parameters [see Fig. 2(b) in Ref. [4]] with $0.60 < \Gamma < 1.08\ e\text{Å}^{-2}$ [4] (see Table I). After subtracting the contribution from the methyl groups ($0.29\ e\text{Å}^{-2}$), the contribution to Γ from water is given by $0.31 < \Gamma < 0.81\ e\text{Å}^{-2}$. For water/octadecyltrichlorosilane (OTS), a similar system, Mezger *et al.* report a hydrophobic gap of 1.1 Å g cm^{-3} [5] which gives a smaller Γ (see Table I) than Ref. [4].

A further contribution to the electron depletion may originate from preferred water orientation in the first interfacial water layer. This would shift the oxygen atoms from the interface and further contribute to the electron density depletion. As suggested by simulations, the oxygen atoms are expected to be in the middle of the first water

TABLE I. δD, ρ_{dep}, ρ_{avg}, and Γ as defined in the text.

System or interface	δD (Å)	ρ_{dep} ($e\text{Å}^{-3}$)	ρ_{avg} ($e\text{Å}^{-3}$)	Γ ($e\text{Å}^{-2}$)
Bulk alkane [6]	2.16	0.047	0.317	0.58
Lipid [7]	4.25	0.185	0.317	0.56
Water/OTE [4] (min)	1.8	0	0.334	0.60
Water/OTE [4] (max)	3.25	0	0.334	1.08
Water/OTS [5]	3.8	0.236	0.326	0.34

layer [9]. In this case, the spacing between these oxygen atoms and the terminal OTE interface is about half the layer spacing of bulk water ($\delta D \simeq 1.25$ Å). In this case, $\delta \rho \simeq 0.334\ e\text{Å}^{-3} \times (8e/10e)$ and gives $\Gamma \simeq 0.33\ e\text{Å}^{-2}$. Such an arrangement of the first oxygen layer is also supported by measurements at the mineral-water interfaces [10], where there is a depleted electron density layer within the first ~ 1.0 Å. Further, this is consistent with the measured depletion range $0.31 < \Gamma < 0.81\ e\text{Å}^{-2}$ provided by our reanalysis above.

In conclusion, accounting for the hydrogen-rich terminal methyl groups of OTE reduces the reported water depletion. Further, the results of Poynor *et al.* [4] *along with* our reanalysis may be consistent with the notion of local water orientation instead of water depletion. Studies which can distinguish between surface water orientation and water depletion would help to elucidate this controversial issue.

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